PB-229 634

# NATIONAL EMISSIONS INVENTORY OF SOURCES AND EMISSIONS OF TITANIUM

GCA Corporation

PREPARED FOR
Environmental Protection Agency

May 1973

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**TECHNICAL REPORT DATA**
*(Please read Instructions on the reverse before completing)*

| 1. REPORT NO. | 2. | PB 229 634 |
|---|---|---|
| EPA-450/3-74-008 | | |

| 4. TITLE AND SUBTITLE | 5. REPORT DATE |
|---|---|
| National Emissions Inventory of Sources and Emissions of Titanium | May 1973 |
| | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>GCA Corporation<br>GCA Technology Division<br>Bedford, Massachusetts 01730 | 10. PROGRAM ELEMENT NO.<br>2AE132 |
| | 11. CONTRACT/GRANT NO.<br>68-02-0601 |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>Environmental Protection Agency<br>Research Triangle Park, N. C. 27711 | 13. TYPE OF REPORT AND PERIOD COVERED<br>Final |
| | 14. SPONSORING AGENCY CODE |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A national inventory of the sources and emissions of the element titanium was conducted. All major sources of titanium-containing emissions were identified and their titanium emissions into the atmosphere estimated. Also, a method for updating the results of the study every two years was recommended.

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U S Department of Commerce
Springfield VA 22151

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| Titanium<br>Air Pollution<br>Emission<br>Inventories<br>Sources | | |

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS *(This Report)* | 21. NO. OF PAGES |
|---|---|---|
| Release Unlimited | Unclassified | 40 |
| | 20. SECURITY CLASS *(This page)* | 22. PRICE |
| | Unclassified | $3.25/1.45 |

EPA Form 2220-1 (9-73)

EPA-450/3-74-008

# NATIONAL EMISSIONS INVENTORY OF SOURCES AND EMISSIONS OF TITANIUM

by

GCA Corporation
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Contract No. 68-02-0601

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Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Water Programs
Office of Air Quality Planning and Standards
Research Triangle Park, N. C. 27711

May 1973

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Publication No. EPA-450/3-74-008

## ACKNOWLEDGEMENT

The continued cooperation and dedication of Mr. Carl Spangler of EPA, who served as Program Monitor until his death, is deeply appreciated.

GCA would like to extend thanks to Mr. David Anderson and Mr. James Southerland of EPA for their cooperation in the preparation of this study.

In addition, special thanks are also due to Mr. W. Wessell, Commodity Specialist, Bureau of Mines, who provided significant technical inputs to this program.

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ABSTRACT

A national inventory of the sources and emissions of the element titanium was conducted. The study included the preparation of an overall material flow chart depicting the quantities of titanium moving from sources of mining and importation through all processing and reprocessing steps to ultimate use and final dispostion. All major sources of titanium-containing emissions were identified and their titanium emissions into the atmosphere estimated. A regional breakdown of these sources and their emissions was also provided. The physical and chemical nature of the titanium-containing emissions was delineated to the extent that information was available, and a methodology recommended for updating the results of the study every two years.

# I. INTRODUCTION

## A. PURPOSE AND SCOPE

The Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards of the U.S. Environmental Protection Agency (EPA) has contracted with GCA Technology Division to conduct a national inventory of the sources and emissions of the element titanium. The purpose of the study was to define as accurately as possible, based on existing and available published and unpublished information, the levels, nature and sources of titanium-containing emissions for defined geographic regions throughout the United States.

The scope of this program is outlined below:

- Develop an overall material flow chart depicting the quantities of titanium moving from sources of mining and importation, through all processing and reprocessing steps to ultimate use and final disposition as far as the movements can be traced.
- Identify all major potential titanium containing emission sources and estimate the total quantity of titanium emitted to the atmosphere from each source. Emission factors and level and types of air pollution control will also be provided for each of these sources to the extent that available information permits.
- Define those sources which contribute at least 80 percent of the total emissions of titanium.
- Provide a regional breakdown of these major sources and their emissions.
- Present the nature of the titanium-containing emissions for each of these major sources including a delineation of their physical and chemical form and particle size distribution to the extent that information is available.
- Provide recommendations as to a methodology for updating the results of this study every two years.

## B. CONCLUSIONS

### 1. Material Flow

Based on all available data, 499,000 tons of titanium were consumed in the U.S. in 1970. As shown in Figure 1, this was almost entirely new metal, with only 7,000 tons of scrap being recycled. The sources of the metal were imports and mining of ilmenite, in approximately equal proportions.

The principal use of titanium was for pigment (79 percent of U.S. total) in the form of titanium dioxide $TiO_2$. Metallurgical processes used most of the remaining 21 percent of the metal. Of the pigment used, slightly more than half was used for paints and related materials. About one fifth of the pigment was used by the paper industry. Several other industries needing a high quality white pigment used the remaining material.

### 2. Principal Emission Sources

Almost 90 percent of the atmospheric emissions of titanium were not associated with the titanium industry, but result from certain emission sources termed "inadvertent" sources. The largest of these is the combustion of large quantities of coal, although coal ash contains only about .07 percent of titanium. The emission of titanium from coal combustion was estimated to be 73,000 tons in 1970, or an amount equal to almost 15 percent of the titanium consumed in 1970.

Within the titanium industry, three sources were identified which contributed a total of only about 2 percent of total U.S. emissions. These were associated with the mining and beneficiation of ilmenite and with the production and consumption of $TiO_2$ pigment. For the most part, these three emission categories were each distributed over fewer than 14 source locations. This compares with between 1000 and 2000 sources of inadvertent emissions.

### 3. Regional Emissions

The region of the U.S. in which most of the estimated titanium is emitted is Region 5 (Ohio and vicinity) which consumes about 40

percent of the nation's coal. Regions 3 and 4 (Pennsylvania to Florida) each contribute about two thirds as much emission as Region 5. The Region having the most emission per square mile is Region 3, followed closely by Region 2 (New York to Virginia).

4. Nature of Emissions

Little information describing titanium emissions was found. Based on the characteristics of the mineral, the metal, and the pigment, in comparison with the processes contributing the emissions, most of the emission is probably in the form $TiO_2$, in particles ranging from 0.1 micrometers up to 10 micrometers. Except for fallout of the largest particles shortly after emission, there is no reason to expect any unusual physical or chemical changes in the emitted particles following emission.

5. Degree of Control

The overall level of control of titanium emission is estimated to have been about 80 percent in 1970. This is largely the result of an estimated 82 percent control of coal burning emissions. The degree of control of the largest emission sources within the titanium industry is variable, ranging from 5 to 90 percent estimated; however, these emissions are a small portion of the U.S. total.

## II. OVERALL U.S. MATERIAL FLOW CHART FOR TITANIUM

Figure 1* presents a flow diagram depicting the total quantities of titanium products moving from sources of mining and importation through the processing and reprocessing steps to ultimate use and final disposition. Each of these sources is discussed below.

### A. ORE PRODUCTION

Ilmenite ($FeO \cdot TiO_2$) is the primary source of domestic titanium. It is found in coastal sands and inland deposits. The only inland mining operation is at Tahawas, New York and accounts for about one-third the total concentrate production[(1)]. The rest comes from coastal dredging operations, located mostly in Florida.

The Tahawas operation is an open pit mine. The ore is extracted by drilling and blasting operations, loaded by electric shovels onto diesel-powered trucks and carried to the beneficiation plant. When the ore is dredged, the resulting slurry is pumped directly to the beneficiating plant.

The beneficiation process at the Tahawas operation involves primary, secondary and tertiary crushing, screening, magnetic separation, grinding and further magnetic separation resulting in a final product which is 45 percent $TiO_2$. Beneficiation of the dredged slurry from coastal operations includes dewatering, cleaning, scrubbing, drying and electrostatic and magnetic separation, and results in a concentrate of over 60% $TiO_2$.

### B. INGOT AND METAL PRODUCTION

Only a small part of the titanium processed in this country goes into metal production. At present all titanium metal and related alloys are processed from rutile. There are experimental investigations of upgrading ilmenite to produce low-grade rutile, but they are currently in the developmental stage. All rutile used in domestic processes is imported, about half being used in metallurgical processes.

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* Note: Data in Figure 1 and in this section are left unrounded, for purposes of information control. On average, the typical statistic is accurate to within 10%, in the opinion of the authors.

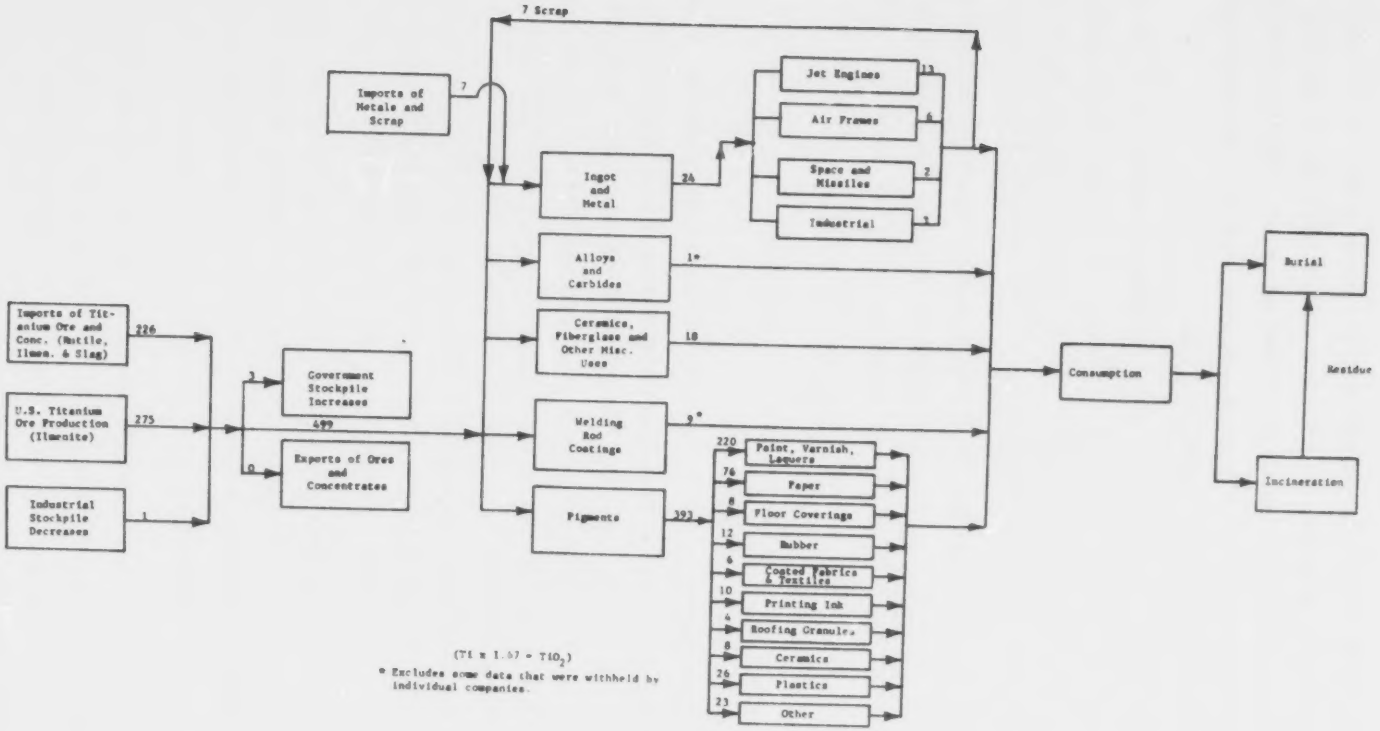


Figure 1. Titanium 1970 Material Flow
(thousand tons contained Ti)

The main method for producing titanium metal is the Kroll process. In the basic process, $TiCl_4$ is reacted with Mg in an inert atmosphere forming Ti metal and $MgCl_2$. Titanium is very susceptible to attack by $N_2$, $O_2$, and $H_2$ at elevated temperatures and an inert atmosphere must be maintained to avoid contamination.

The $TiCl_4$ necessary to this process is produced by passing heated $Cl_2$ gas up through a bed of a mixture of ground rutile and coke resulting in the formation of crude $TiCl_4$ with CO and $CO_2$ as by-products. The $TiCl_4$ is then purified chemically and by partial distillation.

The titanium sponge metal which results from the Kroll process is consolidated primarily by means of arc-melting. The sponge is placed in a water-cooled copper container under an inert atmosphere and heated by an electric arc. The sponge melts, is then cooled forming titanium ingots.

C. ALLOYS AND CARBIDES

Titanium-base alloys are manufactured commercially by adding the alloying metal to titanium sponge during arc-melting. Non-titanium base alloys of Cu, Ni and Ag use $TiH_2$ as a raw material. They are prepared by gradual heating of a mixture of the powdered metal and $TiH_2$ in a vacuum. The $TiH_2$ used in this process is produced by feeding rutile and $CaH_2$ into a furnace with a hydrogen atmosphere at 1830°F. The products, lime and $TiH_2$, are then separated by leaching. The $TiH_2$ is then ground to a powder. The hydrogen is driven off under the vacuum and the resulting titanium metal powder is combined with the base metal of the alloy.

Titanium carbides are prepared by heating $TiO_2$ and carbon in an atmosphere of $H_2$ or in a vacuum. Ferrotitanium master alloys are produced like other ferroalloys and are used in producing ferrotitanium steels.

D. PIGMENTS PRODUCTION

Over 98% of all domestic ilmenite is used for pigment production. Until recently, the major route from concentrated ore to $TiO_2$ pigments was the sulfate process. Another process, the chloride process, has reached a level of equal importance.

In the sulfate process, ilmenite is decomposed by adding sulfuric acid in order to remove the FeO component of the concentrate. The reaction product is dissolved, filtered, hydrolized, filtered again and washed, conditioned, calcined and the resulting $TiO_2$ crystals are ground to the desired pigment size.

The chloride process uses rutile to produce Ti $Cl_4$. This is converted directly to Ti $O_2$ through a vapor phase reaction between Ti $Cl_4$ and steam at 400°C. Solid phase Ti $O_2$ particles precipitate into a dust chamber, are collected and ground to specification.

E. CERAMICS, FIBERGLASS AND OTHER USES

In the production of ceramic material, titanium functions as an opacifier in the frit. The frit is made by fusing various minerals in a smelter and quenching them rapidly in water. This quenching shatters the mixture into small glass particles called frit which are then dried and ground in a ball mill. The primary applications for the frit which contains $TiO_2$ is in enameling iron and steel and in glazing pottery.

Rutile is used in the production of fiberglass. It is added to molten glass in an oven. The glass is then dropped through a small orifice in the bottom of the furnace and blown into filaments which are wound onto a plastic tube and drawn into a smaller diameter.

Ti $Cl_4$ in contact with moist air reacts with the water vapor to form Ti $Cl_4 \cdot 5H_2O$ which on further reaction with water forms titanium hydroxide and HCl. The titanium hydroxide particles are of visible size and quite opaque. This reaction and its resulting visible manifestation makes Ti $Cl_4$ ideal for sky-writing and for smoke screens.

Titanium also finds uses in photography, electronics, and synthetic gem manufacture.

F. WELDING ROD COATINGS

Rutile is also used in welding rod coatings. It is mixed in a slurry and placed in a press with the rod to be coated. The rod and coating are then extruded and fired to drive off the water so that the coating will not explode upon use.

G. REPROCESSING OF TITANIUM METAL

Only the purest scrap titanium can be used. It is melted down in an inert atmosphere by an arc-melting process to form ingots, or embrittled and pulverized in a mercury bath to form a high grade titanium powder.

H. PIGMENT AND METAL CONSUMPTION

Titanium dioxide pigments are blended in an appropriate vehicle in the production of such items as paint, varnish, lacquer, paper, floor coverings, rubber, printing ink, roofing, ceramics, and plastics.

Titanium metal has found extensive use in the aerospace industry in the production of jet engines, air frames, missiles, etc. Because of its susceptibility to attack by nitrogen, oxygen, and hydrogen at elevated temperatures, all casting and joining is done under the protection of an inert atmosphere. In machining and grinding, the titanium must be kept immersed in a coolant to prevent it from fusing with the tool.

$Ti\ O_2$ and Ti O are found in small traces in coal and fuel oil and there are some emissions during the burning of these fuels.

## III. SOURCES AND ESTIMATES OF TITANIUM-CONTAINING EMISSIONS

### A. DATA PRESENTATION AND ACCURACY

Table 1 presents a summary of the data from which titanium emissions were estimated for all major potential sources. Each of the columns comprising this table will be discussed below.

#### 1. Emission Factors

Except where indicated, this gives the pounds of total particulates emitted per ton of production. Such considerations as:

- variations in process conditions among individual plants comprising a source category
- inaccuracies in existing data
- a limited quantity of existing data,

may, however, result in an average emission factor for a source category varying by more than an order of magnitude from the value presented. In recognizing the need to indicate the level of accuracy of these emission factors, a reliability code is presented along with each emission factor value appearing in the Table. This reliability code system is described below and is based on the system utilized in EPA Document No. AP-42, "Compilation of Air Pollutant Emission Factors":

A: (Excellent)

This value is based on field measurements of a large number of sources.

B: Above Average

This value is based on a limited number of field measurements.

C: Average

This value is based on limited data and/or published emission factors where the accuracy is not stated.

TABLE 1

SOURCES AND ESTIMATES OF TITANIUM-CONTAINING EMISSIONS

| | Uncontrolled Particulate Emission Factor (lb/ton) | (kg/kg x $10^3$) | Reliability Code | Production Level (tons/yr) | % $TiO_2$ in Emissions | Reliability Code | $TiO_2$ Emissions Before Controls | Estimated Level of Emission Control | $TiO_2$ Emissions After Controls (tons/yr) |
|---|---|---|---|---|---|---|---|---|---|
| 1. MINING & BENEFICIATION | | | | | | | | | |
| Open Pit Mining | .2 | .1 | (D) | 1,850,000 | 15 | (A) | 30 | 0 | 30 |
| Beneficiation | | | | | | | | | |
| Open Pit | 38 | 19 | (B) | 152,000 | * | (B) | 2,890 | 90 | 289 |
| Dredging | 9.5 | 4.75 | (D) | 308,000 | * | (B) | 1,460 | 90 | 146 |
| 2. METAL PROCESSING | | | | | | | | | |
| Metal Ingots | 0 | 0 | | - | - | | 0 | - | 0 |
| Carbides | 0 | 0 | | - | - | | 0 | - | 0 |
| Alloys: | | | | | | | | | |
| Titanium-Base | 0 | 0 | | - | - | | 0 | - | 0 |
| Ferrotitanium | 150 | 75 | (D) | 5,872 (tons of alloy) | 45% | (C) | 200 | 40% | 120 |
| Steel Production | 25 | 12.5 | (C) | 2,590 ($TiO_2$ consumed as Ferrotit. in steel mfg.) | * | (-) | 31 | 78% | 7 |

TABLE 1. (cont.)

| | Uncontrolled Particulate Emission Factor (lb/ton) | (kg/kg x $10^3$) | Reliability Code | Production Level (tons/yr) | % $TiO_2$ in Emissions | Reliability Code | $TiO_2$ Emissions Before Controls | Estimated Level of Emission Control | $TiO_2$ Emissions After Controls (tons/yr) |
|---|---|---|---|---|---|---|---|---|---|
| 3. OTHER MINERAL USES | | | | | | | | | |
| Welding Rod Coating | 0 | 0 | (D) | - | - | | 0 | - | 0 |
| Ceramics | 16 | 8 | (C) | 370 | * | | 3 | 67% | 1 |
| Fiberglass | 2 | 1 | (C) | 27,000 | * | | 27 | 0% (controls generally not used) | 27 |
| Pigment Production | | | | | | | | | |
| Sulfate Calcining | 150 | 75 | (B) | 344,000 | 100% | (B) | 25,000 | 97% | 750 |
| Grinding | .35 | .175 | (C) | 655,000 | 100% | (A) | 115 | 10% | 104 |
| Drying & Sacking | NA | NA | | 655,000 | 100% | (A) | NA | 99.5% | 3,275 |
| 4. PIGMENT CONSUMPTION | | | | | | | | | |
| Paints, etc. | 15 | 7.5 | (D) | 385,000 | * | | 2,880 | 10% | 2,600 |
| Other Uses | 15 | 7.5 | (D) | 270,000 | * | | 2,020 | 5% | 1,920 |
| 5. INADVERTENT EMISSIONS | | | | | | | | | |
| Coal Burning | NA | NA | | 33,800,000 U.E. | 1.2% | (A) | 405,000 | 82% | 73,000 |
| Coal Cleaning | NA | NA | | 2,000,000 U.E. | 0.12% | (A) | 2,400 | 85% | 360 |

TABLE 1. (cont.)

| | Uncontrolled Particulate Emission Factor (lb/ton) | (kg/kg x $10^3$) | Reliability Code | Production Level (tons/yr) | % $TiO_2$ in Emissions | Reliability Code | $TiO_2$ Emissions Before Controls | Estimated Level of Emission Control | $TiO_2$ Emissions After Controls (tons/yr) |
|---|---|---|---|---|---|---|---|---|---|
| 6. Oil Burning | | | | | | | | | |
| Residual | NA | NA | | 123,000 U.E. | .05% | (A) | 62 | 0 | 62 |
| Distillates | NA | NA | | 146,000 U.E. | .0065% | (B) | 10 | 0 | 10 |
| 7. INCINERATION | NA | NA | | 100,000 U.E. | 4.2% | (B) | 4,200 | 37% | 2,650 |
| 8. Non Metallic Minerals | NA | NA | | 6,900,000 (controlled emissions) | ** | (D) | ** | ** | 3,000 ** |
| U.S. TOTALS | | | | | | | 446,328[1] | | 88,351 |

NA = Not Applicable

U.E. = Uncontrolled Emission

* Emission factor multiplier equal to tons of $TiO_2$ processed or handled annually

** See Text

† Does not include pigment drying and non-metallic minerals

D: Below Average

This emission factor is based on engineering estimates made by knowledgeable personnel.

2. Level of Production Activity

This column depicts the quantity of material produced (unless otherwise stated) annually. When multiplied by the emission factor an estimate of the total particulate emissions for that source in lbs. per year is obtained.

The values in this column are based on the material flow calculations presented in Section II. Consequently, they have the same ± 10% accuracy as do the material flow values.

3. Percent Metal in Emissions

The method of analyzing or assaying a dust sample for the amount of metal it contains determines to a large extent the reliability of the data. For example, analytical chemistry techniques for dust containing substantial fractions of metal can be accurate to within a small percentage. On the other hand, optical spectroscopy methods for determining concentrations on the order of parts per million can be inaccurate by a factor of 2. Because of this variability, the reliability codes discussed above for the emission factors are also utilized to estimate the relative accuracy of the percentage values listed in column 3.

4. Level of Emissions before Control

The values in this column are derived by multiplying the values in columns 1-3. The result is converted to tons/year of emissions before control.

5. Estimated Level of Emission Control

The overall effectiveness of control for a source category is based on two factors:

. the portion of the processes which are under control

. the typical degree of control

For example, if 60% of vertical roasters have some type of particulate emission control, and these include both scrubbers and precipitators such that the apparent weighted average efficiency of control is 85%, the overall control effectiveness is estimated to be 60 x 85 = 51%.

The accuracy of control efficiency data varies with the degree of control. For a wet scrubber operating at 80% efficiency, i.e. passing 20% material, the actual emission may safely be assumed to be between 15 and 25% because of the relative ease of making determinations at this level. Thus the emissions after control may be assumed to be accurate within $\pm$ 5/20 or 25%. On the other hand, for a baghouse reported as being 99% efficient, or passing only 1% of the material, the actual emission may vary from 0.5 to perhaps 2% because it is frequently difficult to make low-level measurements with accuracy. In such a case, the resulting emission data could be in error by a factor of 2.

Unless otherwise specified, it is assumed that the reported overall level of particulate control applies equally to all titanium-containing particles, independent of size, resistance and other important collection parameters. This assumption results in a correct estimate of titanium emissions after control when the particulate is chemically homogenious, i.e., titanium is contained in the same concentration in all particles. If however, titanium is concentrated in certain particles and in addition, the efficiency of the control equipment is not uniform for all particles, then the utilization of an average control level is less valid for calculating titanium emissions after control. Data on the preferential control of titanium-containing particles is seldom available, but is included in this report when possible.

The accuracy of estimating the level of control for a specific category is dependent on the quality of available data. The investigators feel that, in general, the level of control data will contribute an accuracy to the resulting emissions estimates within $\pm$ 25 percent.

6. Level of Metal Emissions After Control

The values in this column are derived by multiplying the values in column 4 by the value (100 minus estimated level of control).

B. DEVELOPMENT OF EMISSIONS ESTIMATES - 1970

Estimates of particulate emissions to the atmosphere in 1970 in the U.S. are developed in the following paragraphs and summarized in Table 1. Table 1 indicates that more titanium emissions result from operations outside the titanium industry than from within the industry. The principal emissions estimates developed in Table 1 are summarized in Section C.

1. Mining and Beneficiation

No emission factors for the drilling, blasting, and loading of titanium ore were found. A figure of 0.2 lbs/ton emission developed in other hard-rock mining operations is used in place of direct data.[2] On the basis of 15 percent $TiO_2$ in the rock and no control of the mining emissions,[1] the estimated release of titanium to the atmosphere is 30 tons per year. The Tahawas mine in New York, the only open pit mine in the U.S., accounts for about one-third of the ilmenite mined in the U.S. The remainder, produced by dredging, entails low emissions as it is largely a wet process. A conservative emission factor of 25 percent of the factor for the open pit mine was assumed.

Beneficiating operations are reported to involve the following emission factors:[1]

- crushing, screening, fines milling recrushing & rescreening
- conveying, general screening and handling
- drying.

An overall emission factor of 38 lbs. of particulate per ton of ilmenite produced (46% $TiO_2$) is estimated from data provided by an ilmenite producer.[1] This factor, however, applies only to hard-rock beneficiation. It is estimated that only about 25 percent as much emission results from the beneficiation of dredged materials, as there are no

crushing and screening operations as in the mining of hard rock. A 90 percent level of emissions control was also assumed for these beneficiation processes. The resulting estimated net emission to the atmosphere by beneficiation is about 435 tons.

2. Metal Processing

a. Metal and Ingot Production

The major process involving titanium metal production is the Kroll process which has two steps; the production of $TiCl_4$ using the fluidized bed method, and the reduction of $TiCl_4$ by Mg to form $MgCl_2$ and Ti sponge. The sponge is then consolidated to form the solid metal. The production of $TiCl_4$ is assumed to be well controlled as chlorine gas would escape in large quantities if it were not. The reduction and consolidation steps are done under the protection of an inert atmosphere and are also assumed to be clean.

b. Titanium-Base Alloys and Carbides

Titanium-base alloys are produced in an inert atmosphere and emissions are again assumed to be negligible.

c. Ferrotitanium

Figure 2 indicates that in the case of ferrosilicon production, the greater the concentration of silicon the greater the emission. Lacking better data, one can assume that the same data applies to ferrotitanium production. Using the typical titanium content of 27 percent, an emission of 150 lbs/ton is estimated.[4] Of this, 27 percent is assumed to be titanium, or 40 lbs/ton, equivalent to 67 lbs/ton of $TiO_2$. A production estimate of 5,872 tons in 1970 is based on the reported consumption of ferrotitanium in steel production.[4] This results in 200 tons before control, or 120 tons after an estimated 40 percent control.[5]

d. Steel Production

Using the figure for total annual ferrotitanium use in steel production and a weighted emission factor developed along with a weighted level of control:

Tonnage of Ferrotitanium used in steel: 5,872[4]

Emission Factor: 25 lbs. ferrotitanium emissions/ton[5] ferrotitanium utilized

Level of control: 78%

There results an estimated emission after control of only 7 tons.

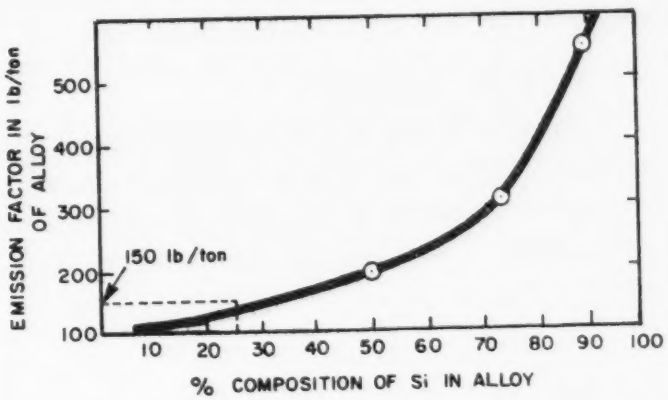


Figure 2. Emission of Particulate in Ferrosilicon Production (Reference 3)

Little data is available on the titanium content of particulate from the principal iron and steel processes. Open hearth fumes are reported to contain 0.17 percent titanium; and electric furnace fumes, 0.03 percent titanium.[6] These data would produce estimates of about 1000 and 9 tons of $TiO_2$ emission per year, respectively. These estimates are not included in Table 1 because of the tentative and incomplete nature of the data, the other iron and steel processes being unrepresented. Further investigation of titanium emissions from these sources is recommended.

e. Metal Fabrication

Atmospheric emissions are assumed to be negligible, as all forging, casting, and joining of titanium is done under an inert

atmosphere and most machining is done in the presence of a liquid coolant which would capture most of the potential emissions.

3. Other Basic Processes

a. Welding Rod Coatings

This involves utilizing rutile in a wet slurry and gradual drying to slowly remove the water without cracking the coating. Titanium compound emissions are again assumed to be zero.

b. Ceramics

The mineral equivalent to approximately 370 tons of $TiO_2$ was used to opacify frit. Using an uncontrolled emission factor of 16 lbs/ton[3], the total uncontrolled $TiO_2$ emission is estimated to be 3 tons. Using a conservative control estimate of 2/3 gives a controlled emission estimate of 1 ton of $TiO_2$.

c. Fiberglass

The major particulate emissions in fiberglass manufacture are from the glass melting oven. $TiO_2$ is added to already melted glass in the oven. Generally no controls are used. Uncontrolled emission factors are:

1 lb/ton: recuperative heat exchanger
3 lb/ton: regenerative heat exchanger[5]

An average factor of 2 lbs/ton is assumed. Consumption figures of $TiO_2$ for fiberglass are not available, but it is assumed that 90 percent of the "ceramics, fiberglass and other miscellaneous uses" category in Figure 1 is for fiberglass, or approximately 27,000 tons $TiO_2$. Estimated $TiO_2$ emissions therefore are 27 tons.

d. Pigments Productions

Nearly all emission from pigment production is from the calcining and subsequent grinding operations, and hence is practically 100 percent $TiO_2$. Of the two processes used in the production of titanium pigment, the sulphate process contributes a little over half of the production (52.5%).[7] The essential difference in this process is the

added step of calcining in producing $TiO_2$. Reports of emissions tests of titanium pigment calciners indicate 30 to 230 lbs/ton before control, with an average of 150 lbs/ton.(8) The calciner controls reported average about 97% efficiency.

The chloride process is closed up to this point, and it is assumed that any particulate emissions from the process are negligible. Subsequently, the pigment from both processes is ground, dried, and sacked. The grinding operation is relatively closed, producing only 0.35 lbs/ton before control.(5) Because little dust is generated, control measures are limited to an estimated 10 percent, resulting in an estimated 55 tons of $TiO_2$ emission to the atmosphere. In the spray drying process, it is evident that all of the material is at one time an aerosol. Test reports range from 90 to 99.9 percent control, a range of two orders of magnitude in the effect on emission estimates.(8) It is assumed here that 0.5 percent of the product escapes the control measures which are used on every drier, resulting in an emission estimate of 3,275 tons. It is further assumed that the sacking process is sufficiently integrated with the dryer and its emission control equipment, that the above estimate applies to the overall process.

e. Miscellaneous

$TiO_2$ also finds uses in artificial gem manufacture, photographic plates, sky writing, and smoke screens. Only the last two contribute any real emissions. These are such a small percentage of the total they are neglected here.

4. Pigment Consumption

a. Paint, Varnish, Lacquer, and Ink

In the EPA emissions manual, two processes involving pigment use are paint and ink production. Both processes involve grinding the pigment into the vehicle, and the emission estimates are identical. There are no chemical reactions involved. Most of the emission is due to handling the dry pigment, and is estimated at 0.5 to 1.0 percent of the pigment used.(3) At a rate of 0.75 percent (15 lbs/ton) and a paint and

ink pigment consumption of 384,000 tons of $TiO_2$, the emission estimate before control is 2880 tons. Control of the pigment handling processes is estimated at 10 percent, resulting in a net emission of 2600 tons.

b. Other Pigment Consumption

The other processes using pigments, indicated in Figure 1, are all basically similar to the above, i.e. all involve mixing a dry pigment into a material to be colored. Using the same emission factor, a consumption of 270,000 tons of $TiO_2$, and an estimated control effectiveness one half that for paint production because of the miscellaneous nature of the processes, the net emission is estimated to be 1920 tons.

5. Inadvertent Sources

a. Coal Combustion

Coal consumption in 1970 amounted to about 517,000,000 tons.[4] The particulate generated has been estimated at 33,800,000 tons, of which 82% was controlled, leaving 6,100,000 tons of emission to the atmosphere.[5] Thus, even a small concentration of titanium in the coal flyash would result in a large net emission of titanium. This concentration figure is reported to be 0.72 percent (= 1.2% $TiO_2$) based on spectrochemical analyses of 373 different samples of coal from across the U.S.[9] The net estimated emission of titanium from this source is 73,000 tons of $TiO_2$ in 1970, the largest estimate in this study.

b. Coal Cleaning

Subsequent to mining, coal is crushed, segregated, washed, and dried, and in this last process emissions are estimated to be about 300,000 tons per year.[5] This is after control at an estimated 85 percent,[5] resulting in a before-control emission estimate of about 2,000,000 tons per year. At a 10 percent ash content of coal and 1.2 percent in $TiO_2$ in the ash, this is equivalent to 360 tons of $TiO_2$ emitted to the atmosphere.

c. Oil Combustion

There are traces of titanium in residential and commercial grade fuels, .004 percent according to "Emissions from Fuel Oil

Combustion", and 0.03% in residual utilities fuels, according to the same source.[10] These are equivalent to .0065 and .05% $TiO_2$, respectively.

Emission figures have been developed for fuel oil burning. Emissions from residual, industrial and electric utilities amount to 123,000 tons while emissions from residential and commercial use are 146,000 tons.[2] Both sources are uncontrolled, resulting in emissions of 62 and 10 tons of $TiO_2$, respectively.

d. Incineration

The fly ash from typical municiple incinerators contains a great deal of mineral particulate matter of which an estimated 4.2% is $TiO_2$.[11] Total estimated mineral particulate emissions from incinerators in 1970 was about 100,000 tons.[12] According to the same source, total mineral particulate emissions from incinerator stacks was about 63,000 tons, indicating 37% control. This results in an estimated 2,650 tons of $TiO_2$ released by incineration.

e. Non-metallic Mineral Production

Emissions after control equipment have been estimated as follows for a variety of major U.S. industries.[5]

| | |
|---|---|
| Crushed stone (about 0.5%) | $4.6 \times 10^6$ TPY |
| Cement | $0.9 \times 10^6$ TPY |
| Lime | $0.6 \times 10^6$ TPY |
| Clay | $0.5 \times 10^6$ TPY |
| Fertilizers | $0.3 \times 10^6$ TPY |
| Total | $6.9 \times 10^6$ TPY |

No analyses of these particulates for titanium content were found except in the case of cement, which was approximately 0.01 percent.[6] However the earth's crust is reported to contain about 0.44 percent titanium.[13] Applying these percentages to the total emission above results in an estimated titanium emission range of 690 to 30,000 tons per year. Table 1 includes a token emission of 3,000 tons of $TiO_2$, with an accompanying indication that the estimate is a weak one needing further investigation.

## C. SUMMARY OF PRINCIPAL EMISSIONS

Table 2 summarizes the major sources and estimated emissions of titanium, as developed in Table 1 and the accompanying discussion. The sources are grouped in two categories, those directly originating with the industries using titanium as a material; and inadvertent sources. The latter category is by far the larger, due to the small but significant amount of titanium contained in domestic coals.

TABLE 2

SUMMARY OF PRINCIPAL SOURCES AND EMISSIONS - TITANIUM

| Inadvertent Sources | U.S. Tons/Year of Equiv. $TiO_2$ | % of U.S. |
|---|---|---|
| Coal Burning | 73,000 | 82.6 |
| Non-Metallic Minerals | (3,000 est.) | 3.4 |
| Incineration | 2,650 | 3.0 |
| **Titanium Industry Sources** | | |
| Pigment consumption | 4,520 | 5.1 |
| Pigment production | 4,080 | 4.6 |
| Beneficiation of ore | 465 | 0.5 |
| | | 99.2 |

## IV. REGIONAL DISTRIBUTION OF PRINCIPAL SOURCES AND EMISSIONS

For purpose of showing geographical distribution, the U. S. was divided into ten regions identical to the Regional Branches of EPA:

| Region | |
|---|---|
| I | Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, Vermont |
| II | New Jersey, New York, Puerto Rico, Virgin Island |
| III | Delaware, Maryland, Pennsylvania, Virginia, West Virginia, District of Columbia |
| IV | Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, Tennessee |
| V | Illinois, Indiana, Michigan, Minnesota, Ohio, Wisconsin |
| VI | Arkansas, Louisiana, New Mexico, Oklahoma, Texas |
| VII | Iowa, Kansas, Missouri, Nebraska |
| VIII | Colorado, Montana, North Dakota, South Dakota, Utah, Wyoming |
| IX | Arizona, California, Nevada, Hawaii, and the South Pacific |
| X | Alaska, Idaho, Oregon, Washington |

Emissions from the principal sources listed in Table 2 are distributed among these ten regions, as shown in Table 3. Also the number of plants producing the emissions is shown in the table when such information was available.

The accuracy of the distributions by region varies with the category. The number of plants per category ranged from one to several thousand in this study. When the number of plants was less than 100, an attempt was made to identify each plant and plant location, and include it in one of the ten regions. When production or capacity figures for these plants were available, total production or capacity for each region was computed, and the U. S. emission estimate for that category was distributed by region accordingly. When production or capacity figures were not available, the emission was distributed by the number of plants in each region. If the

TABLE 3

REGIONAL DISTRIBUTION OF PRINCIPAL SOURCES AND EMISSIONS

| Principal Sources | EPA Region 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Total (units) Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Inadvertent Sources | | | | | | | | | | | |
| Coal burning | 0.7<br>510 | 5.7<br>4160 | 21.7<br>15840 | 21.0<br>15330 | 41.1<br>30000 | 1.4<br>1020 | 4.1<br>3000 | 3.3<br>2410 | 0.7<br>510 | 0.3<br>220 | 100% (Coal shipped) (4)<br>73,000 (TPY) |
| Non-metallic minerals | 5.8<br>174 | 12.5<br>375 | 11.5<br>345 | 15.7<br>470 | 21.6<br>650 | 10.0<br>300 | 5.5<br>165 | 2.7<br>81 | 11.3<br>340 | 3.2<br>96 | 100% (Population) (14)<br>(3,000) (TPY) |
| Incineration | 16.6<br>440 | 24.2<br>640 | 17.7<br>470 | 11.8<br>312 | 24.0<br>635 | 3.5<br>93 | 1.4<br>37 | 0.3<br>8 | 0.5<br>11 | 0<br>0 | 100% (Incin. Capacity) (12)<br>2,650 (TPY) |
| Titanium Industry Sources | | | | | | | | | | | |
| Pigment | 0<br>0 | 27<br>1220 | 28<br>1270 | 23<br>1040 | 5.4<br>245 | 0<br>0 | 13.3<br>600 | 0<br>0 | 3.3<br>150 | 0<br>0 | 100% (Pigment Production) (15)<br>4,520 (TPY) |
| Pigment production | 0<br>0 | 3<br>1100 | 6<br>1220 | 3<br>840 | 3<br>200 | 0<br>0 | 1<br>610 | 0<br>0 | 1<br>110 | 0<br>0 | 17 (Plants) (15)<br>4,080 (TPY) |
| Beneficiation of ore | 0<br>0 | 2<br>349 | 1<br>29 | 3<br>87 | 0<br>0 | 0<br>0 | 0<br>0 | 0<br>0 | 0<br>0 | 0<br>0 | 6 (Plants) (4)<br>465 (TPY) |
| Totals | 1124 | 7844 | 19174 | 18079 | 31730 | 1413 | 4412 | 2499 | 1121 | 316 | 87,715 (TPY)* |
| | 1.3 | 8.9 | 21.6 | 20.5 | 35.8 | 1.6 | 5.0 | 2.8 | 1.3 | 0.4 | 99.2 (% of U.S.) |

*Tons per year, $TiO_2$, emitted to the atmosphere

number of plants was very small or there was reason to believe that certain plants were larger or produced more emission, distributions were weighted accordingly.

On the other hand, when the estimated number of plants was greater than about 100, and the distribution of plants was not known, the regional breakdown was made on a different basis, such as population, geographical area, or shipments reported, as most appropriate for that category. Whether the distribution was by plant size, number of plants, or another statistic, the distribution is believed to be accurate to within 10 percent in most cases.

The basis for the Table 3 distribution of the inadvertent (i.e. non-titanium industry) sources is: coal combustion, according to shipments of coal by states of destination; non-metallic production, by population; and incineration, by reported incinerator capacities per state. As discussed earlier, the estimate for non-metallic mineral production is weak and needs further investigation.

Titanium industry emission sources are distributed as follows:

- emissions from pigment production are distributed by region, according to the reported total plant capacity in that region.[15]

| Region: | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Total (TPY) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sulphate Capacity: | 0 | 133 | 164 | 46 | 12 | 0 | 108 | 0 | 0 | 0 | 463,000 |
| Chloride Capacity: | 0 | 87 | 68 | 144 | 32 | 0 | 0 | 0 | 27 | 0 | 358,000 |
| | | | | | | | | | | | 821,000 (TPY) |

- Due to a lack of capacity data, emissions from the five beneficiation plants which produce ilmenite from beach sands were all assumed to be equal; i.e., 146 ÷ 5 = 29 tons/year.

- There is only one open pit ilmenite mine in the U. S., in Tahawas, New York, and so all emissions from open pit mining were allocated to Region 2.

- Pigment consumption is assumed to be distributed according to pigment production, because the largest fraction of the pigment consumed is for paint, and most of the companies producing the pigment are paint companies. It is in effect assumed that the consumers of pigment for other than paint uses are located near the pigment producers.

The overall distribution by region is also shown in Table 3, with Region 5 estimated to produce the most emissions of titanium followed by Regions 3 and 4. These are the coal consuming regions of the U. S. Table 3 is strongly weighted by the single emission from coal combustion, in the absence of which, Region 2 would be first with the most emission.

Considering the geographical areas of these regions, Region 3 produces the most emission per square mile (0.16 tons per square mile-year) followed closely by Region 2.

## V. NATURE OF EMISSIONS

The emissions of titanium and titanium dioxide are largely dependent on their properties, shown in Table 4.

TABLE 4

PHYSICAL PROPERTIES OF Ti and $TiO_2$*

| | Ti | $TiO_2$ |
|---|---|---|
| Melting Point | 1668°C | 1640°C |
| Boiling Point | 3260°C | 2700°C |
| Density | 4.51 g/cc | 4.2 g/cc |
| Atomic Weight | 47.9 a.w.u. | 79.9 a.w.u. |
| Heat of Vaporization | 106.5 kg-cal/g-atom | ---- |
| Mineral hardness, ILMENITE: | 5.5, std. minerology scale. | ($=FeO \cdot TiO_2$). |

Probably the most important property from the emissions standpoint is the boiling, or vaporization point, which is substantially higher than the combustion temperatures of coal or incinerator refuse. This indicates that the emission in both cases probably has the same physical and chemical form as the feed material. In fact, this is probably true of nearly all the principal emissions discussed above.

Beneficiating and non-metallic mineral operations involve mechanical pulverization and in this type of process the hardness of the material affects the fineness of any particles produced. Because ilmenite is a moderately hard material, the pulverization must be an intense process producing a moderate amount of fine particles. Hard-rock mining of ilmenite is estimated to produce particles of 5 micrometers average diameter, ranging from 1/2 to 10 micrometers.[1] The upper size limit is a strong function of the distance from the source.

Pigment handling processes, including incineration of paper containing titanium oxide pigment coatings, will produce emissions of $TiO_2$ particles

* Perry's Chemical Engineers Handbook, 4th Edition, Table 3-169.[16]

somewhat dependent on the particle size. One pigment manufacturer estimated for this study that the pigment produced is 0.1 to 1.0 micrometer in diameter, with an average diameter of 1/4 micrometers.[1] Another estimate gives nearly all particles being under 0.2 micrometers, with about 2 percent ranging up to 0.40 micrometers.[17] The size of the pigments produced varies with the market.

Fine particles, those 1 micrometer diameter and smaller, may be expected to travel considerable distances before being deposited or being washed out of the air by natural processes. About 9.8 percent of the total U.S. emission of $TiO_2$ is as pigments most of which is in particles smaller than 1 micrometer. Thus the emissions of pigment probably contribute to the average ambient titanium concentration in the U.S. In addition, the combustion of distillate oils, and of gasoline (.01 to 0.1 ppm Ti content)[18] which produce more finely divided particulate, may influence background air quality despite the smaller total mass emitted.

There is no reason to suspect any unusual activity of titanium-containing particles following emission, including agglomeration or chemical reaction with atmospheric components in the cases of some particulate. It appears that $TiO_2$ is a relatively stable and unreactive material in all respects.

$TiO_2$ has recently been approved as a food additive by the Food and Drug Administration, and has been used for some time as a cosmetic. Its common use as a brightener of domestic papers is further indication that $TiO_2$ is considered not harmful.

## VI. UPDATING OF EMISSIONS ESTIMATES

The following recommendations are made for periodically updating the estimates made in this study:

### A. VERIFICATION OF CURRENT ESTIMATES

1. Verify that the fraction of titanium contained in flyash from stacks of coal combustion plants is essentially unchanged from the fraction contained in coal ash produced in laboratory analyses of coal samples.[9] There is no reason to suspect any substantial change. However, the assumption that there is no change has strong bearing on the conclusions of this program.

2. Determine a better average titanium concentration for the emissions generated by the non-metallic minerals industry, in particular from crushed stone.

3. Verify the relatively low emissions control practices of the pigment producing and consumption industries, and of the ilmenite beneficiating plants.

### B. PERIODIC REVIEW OF ESTIMATES

1. The Bureau of Mines estimates for material flow, industry practices, and trends provide the best estimates of the size of the industry.

2. EPA activities are currently generating the best emissions data and should be reviewed:

   a. Overall industry studies, e.g. References (19).

   b. The Source Test Program, in which specific individual plant emissions are measured. This information provides emission factors

for specific examples of typical industry operations, and also provides some analyses of the particulate usually including trace metal content and particle size.

c. NEDS (National Emissions Data System) is steadily being enlarged and improved. This system can provide emission factors for specific plants and plant operations, the type of particulate control equipment in use, and the actual, or estimated, control efficiency. The system may eventually be expanded to include description of the emissions.

3. The titanium industry should be consulted for its opinion and suggestions on the most recently published estimates. This may be best accomplished by interviewing the Titanium Commodity Specialist, Division of Nonferrous Metals, Bureau of Mines in Washington; or, interviewing one or more of the principal companies in the industry.

4. Literature should be reviewed, using (a) industrial views as published from time to time in Chemical Engineering, for example, and (b) environmental views as summarized in Pollution Abstracts, for example.

5. Individual companies or plants may be approached for opinions, data, or cooperative tests of their own operations. It is difficult to obtain fresh information in this way, due to the natural reluctance of plants to discuss environmental problems. However, data thus obtained have a relatively high degree of reliability.

6. State agencies in which specific plants are located may be able to provide useful information, and should be contacted.

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